

QUEENSLAND DEPARTMENT OF PRIMARY INDUSTRIES

DIVISION OF PLANT INDUSTRY BULLETIN No. 341

**PARTITION CHROMATOGRAPHY OF
TRICHLORPHON**

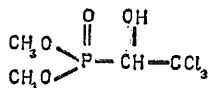
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SUMMARY

The partition properties of trichlorphon between water and carbon tetrachloride were investigated. From the results obtained, using carbon tetrachloride and chloroform as the mobile phase and water as the stationary phase, a partition column was developed. Separation of trichlorphon from other components of formulations was readily achieved on such a column.

Introduction

Trichlorphon (O, O-dimethyl (1-hydroxy-2, 2, 2-trichloroethyl) phosphonate), with the structure



is a compound of high insecticidal activity. In order to estimate its concentration in formulations, it is desirable that it should be separated from other constituents present in the mixture. Normally such constituents are surface active agents and solvents.

After separation, trichlorphon may be estimated by various methods. Giang and Caswell (1957) used polarography, while Giang, Barthel, and Hall (1954) determined trichlorphon colorimetrically by a modified Fujiwara reaction, after hydrolysis to chloroform.

If the trichlorphon could be isolated quantitatively from the formulation, it could be estimated gravimetrically.

A separation from other constituents of the mixture would also be very useful for examining formulations in which trichlorphon has partially decomposed.

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Perhaps the most general method of separating an organic pesticide from the remainder of the formulation involves the use of adsorption chromatography. Because trichlorphon contains a hydroxyl group it is quite polar and is not well suited to quantitative recovery from an adsorbent.

The compound has interesting solubility properties. It is soluble in water because of the secondary alcohol group and also soluble in the common organic solvents such as ether and acetone. The chlorinated solvents dissolve trichlorphon and it is especially soluble in chloroform (possibly caused by the $-CCl_3$ group).

This paper presents a study of the partition chromatography of trichlorphon, using carbon tetrachloride and chloroform as the mobile phase and water as the stationary phase.

Results

Distribution between water and carbon tetrachloride.—The distribution ratio (D) may be defined (Morrison and Freiser 1957, p. 10) as

$$D = \frac{\text{conc. of solute in solvent A}}{\text{conc. of solute in solvent B}}$$

A preliminary study of the distribution ratios for trichlorphon between several organic solvents and water revealed that carbon tetrachloride would probably be the best solvent for use as a mobile phase in a partition column.

A detailed relation between the concentration of trichlorphon in carbon tetrachloride and that in water at $22 \pm 2^\circ\text{C}$ was experimentally determined. This relation is shown in Figure 1.

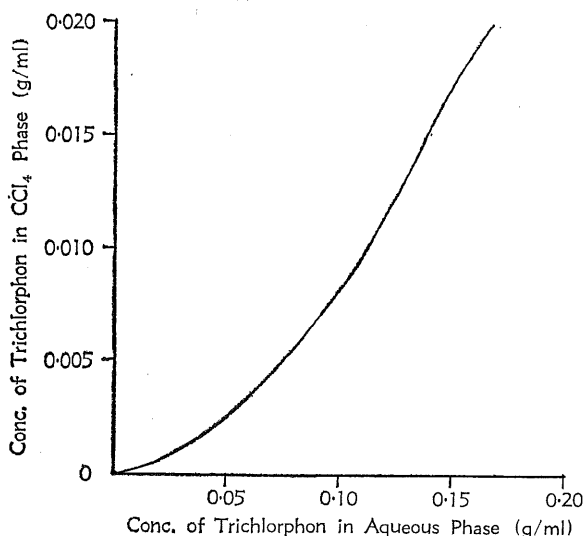


Fig. 1.—Relation between concentration of trichlorphon in carbon tetrachloride and in water at $22 \pm 2^\circ\text{C}$.

It is seen that the relation is non-linear; this is probably caused by the different degrees of association of the solute in the two solvents. Lorenz, Henglein, and Schroder (1955) report that trichlorphon exists in an associated form.

A plot of D v. concentration of trichlorphon in water is shown in Figure 2, where

$$D = \frac{\text{conc. of trichlorphon in water}}{\text{conc. of trichlorphon in carbon tetrachloride}}$$

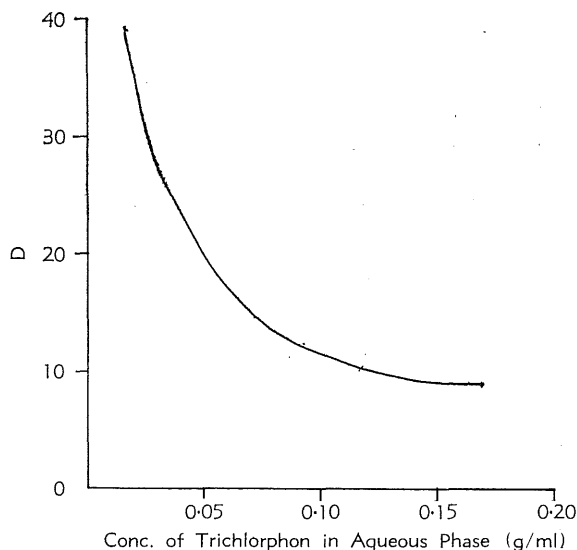


Fig. 2.—Relation between distribution ratio (D) of the solute between water and carbon tetrachloride and the concentration of trichlorphon in water.

It will be seen that at relatively high concentrations of trichlorphon, the value of D tends to a constant value; at low concentrations D approaches infinity.

Partition column.—A partition column was constructed by supporting water on silicic acid as the stationary phase and eluting with carbon tetrachloride as the mobile phase.

Using the well-known relation;

$$V_r = V_o (1 + \frac{b}{a} D)$$

it is possible to calculate the retention volume on the column, where

V_r is the retention volume, i.e. the volume of solvent required to elute the solute;

V_o is the volume of the mobile phase in the column;

b is the cross-sectional area of the stationary phase in the column;

a is the cross-sectional area of the mobile phase in the column;

D is the distribution ratio of the solute between the stationary and the mobile phases.

In the column prepared,

$$V_o = 9.5 \text{ ml}$$

$$b/a = 0.43.$$

In the case of trichlorphon, the front of the eluted band should begin to leave the column quite sharply, since, if any solute travels far ahead of the main band, it will be at a lower concentration. At this lower concentration, as may be seen from Figure 2, D increases and thus the solute will tend to remain in the aqueous stationary phase. Thus the relation between D and concentration will tend to stop any "streaking" ahead of the main band.

The value of D may be taken as being about 10 for calculation of the retention volume of the front of the band, so that

$$V_r = 9.5 (1 + (0.43 \times 10)) = 50 \text{ ml.}$$

Because of the non-linear partition (Figure 2), any solute which falls behind the main band will be even further retarded. As it becomes more dilute, the proportion held in the stationary phase becomes larger; this process results in an extreme "tailing."

The elution profile using carbon tetrachloride as mobile phase is shown in Figure 3.

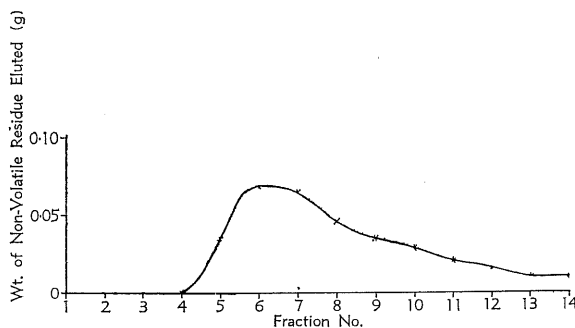


Fig. 3.—Elution profile with carbon tetrachloride as the mobile phase.

Most relatively non-polar organic substances are either insoluble or practically insoluble in water, and therefore will have very low D values. Calculation of retention volumes shows that such compounds should be eluted in the first 20 ml passed through the column. They could be retained longer, however, by the absorptive properties of the silicic acid, but using the column described, these have been reduced to a minimum by the high water content.

To prevent the "tailing" of the trichlorphon band, a solvent with a low distribution ratio for trichlorphon between water and itself was required. Chloroform was admirably suited to this purpose.

It was decided to commence development with chloroform as soon as the trichlorphon had appeared in the eluate. Use of the same column as previously, but development with 50 ml carbon tetrachloride, then 10 ml of 1 : 1 mixture of carbon tetrachloride and chloroform followed by development with pure chloroform, produced the curve shown in Figure 4.

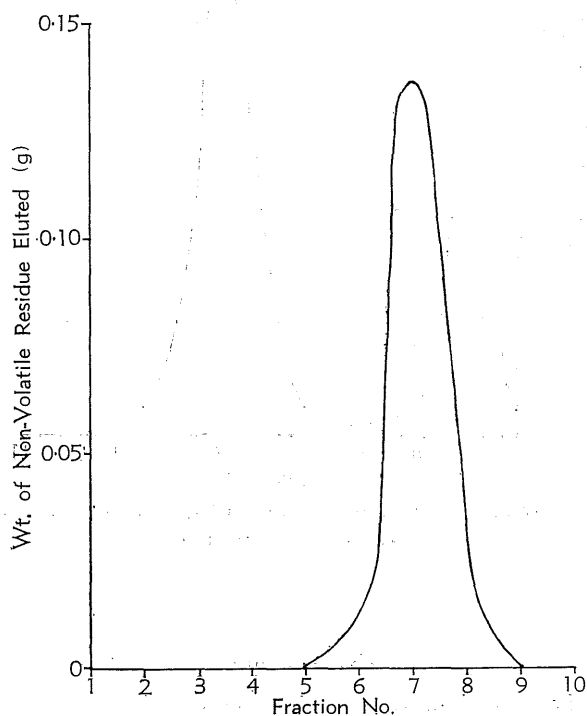


Fig. 4.—Elution profile with carbon tetrachloride, followed by carbon tetrachloride/chloroform, then chloroform.

This is a more satisfactory shape of band and affords quantitative recovery of added trichlorphon.

Surface active agents and detergents are held firmly in the aqueous layer and do not interfere with the collection of trichlorphon.

A commercial sample of a trichlorphon formulation was chromatographed under the conditions described. The weight of non-volatile residue collected in each fraction is shown in Figure 5.

It is seen that other organic material present is collected in the first 30 ml of solvent eluted, followed by trichlorphon from 50-90 ml. By collection of the appropriate fractions, the trichlorphon may be recovered quantitatively from the column.

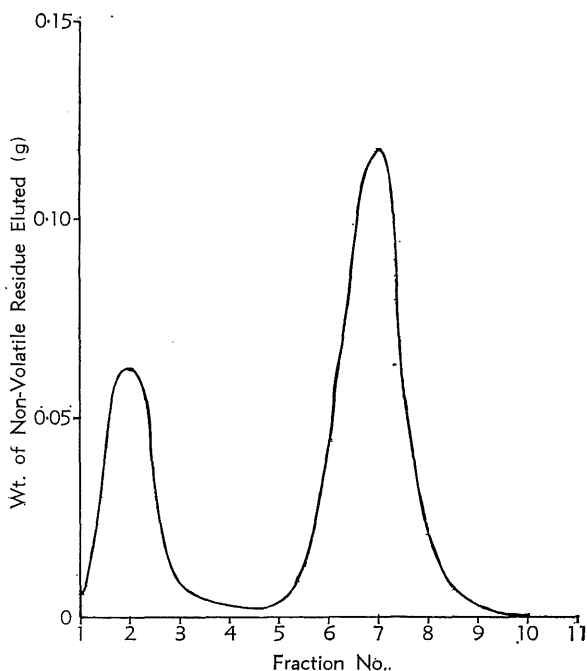


Fig. 5.—Non-volatile residues of a commercial sample of a trichlorophon formulation collected in each fraction.

Experimental

Reagents.—The following reagents were used:

Carbon tetrachloride.—Laboratory reagent grade was used throughout the experiment. Before use it was saturated by shaking with a small volume of water and allowing the phases to separate.

Chloroform.—B.P. reagent grade was distilled through sodium thiosulphate solution to remove phosgene, hydrochloric acid and ethanol. For chromatography, it was saturated with water by the same method as described for carbon tetrachloride.

Trichlorophon.—This was recrystallized from a benzene/petroleum ether mixture, m.p. 78-80°C.

Silicic acid.—“Mallinckrodt” analytical reagent, 100 mesh, No. 2847, was dried at 135°C for at least 3 hr. To 10 g silicic acid was added 7 ml water and the mixture was shaken and stirred until a homogeneous powder resulted.

Acid-washed sand.

Apparatus.—Chromatographic tubes (1.9 cm i.d.) fitted with teflon stopcocks were used for all chromatography.

Determination of distribution between water and carbon tetrachloride.—Weighed amounts of trichlorphon were added to stoppered test-tubes containing known volumes of water and carbon tetrachloride. The tubes were then shaken and let stand for 24 hr at $22 \pm 2^\circ\text{C}$.

Aliquots of the carbon tetrachloride phases were pipetted into weighed test-tubes. The solvent was evaporated under a stream of nitrogen on a steam-bath, then in a vacuum desiccator. This procedure was repeated until constant weight was obtained. From these data, concentrations in aqueous and organic phases were calculated. These values are shown graphically in Figure 1.

Partition column.—Wet silicic acid (10 g) was slurred with carbon tetrachloride and the mixture was poured into the chromatographic tube. After allowing the silicic acid to settle, a layer of sand was placed on the top to prevent any disturbance of the support during further addition of solvent.

By weighing the column before and after packing, the following parameters were obtained:

Mass of silicic acid acting as support for the stationary phase, 5.9 g.

Volume of water on the column, 4.1 ml.

Volume of carbon tetrachloride on the column, 9.5 ml.

The trichlorphon was taken up in a small volume of carbon tetrachloride and transferred quantitatively to the top of the column. Collection of 10-ml fractions of eluate in weighed test-tubes was begun immediately and was continued throughout a run.

Evaporation of the solvent in each fraction to constant weight was carried out as described above.

Not more than 0.2 g trichlorphon was chromatographed during any one run.

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